

CLAIMS

We claim:

1. A process for at least partially removing from a product stream comprising C_x olefin wherein x is an integer ranging from 2 to 6, an oxygenate impurity selected from dimethyl ether, diethyl ether, di-n-propyl ether, diisopropyl ether, methylethyl ether, methyl-n-propyl ether, methylisopropyl ether, ethyl-n-propyl ether, ethylisopropyl ether and n-propylisopropyl ether, which comprises:
converting said oxygenate impurity to a compound whose boiling point differs by at least about 5°C from said oxygenate impurity; and
separating at least some of said compound from said C_x olefin.
2. The process of claim 1 wherein said oxygenate impurity is dimethyl ether.
3. The process of claim 2 wherein said product stream comprises at least about 1 mppm dimethyl ether.
4. The process of claim 2 wherein said product stream comprises at least about 2.5 wt% dimethyl ether.
5. The process of claim 2 wherein said separating provides an oxygenate impurity-depleted stream which comprises no greater than about 100 mppm dimethyl ether.
6. The process of claim 2 wherein said separating provides an oxygenate impurity-depleted stream which comprises no greater than about 50 mppm dimethyl ether.
7. The process of claim 2 wherein said separating provides an oxygenate impurity-depleted stream which comprises no greater than about 10 mppm dimethyl ether.

8. The process of claim 2 wherein said separating provides an oxygenate impurity-depleted stream which comprises no greater than about 1 mppm dimethyl ether.
9. The process of claim 2 wherein said product stream comprises propylene.
10. The process of claim 1 wherein said separating is carried out by fractionating in a distillation column.
11. The process of claim 1 wherein said converting is carried out without substantially converting said C_x olefin.
12. The process of claim 1 wherein said converting is carried out in the absence of added hydrogen.
13. The process of claim 1 wherein said converting is carried out in the presence of added hydrogen.
14. The process of claim 1 wherein said product stream comprises at least one member selected from the group consisting of methanol, water, CO and CO₂, wherein said product stream is treated to remove at least some of said member, prior to said converting.
15. The process of claim 1 wherein said product stream containing said oxygenate impurity is derived from a process which converts oxygenates to olefins.
16. The process of claim 1 wherein said boiling point differs by at least about 10°C.

17. The process of claim 1 wherein said boiling point differs by at least about 50°C.

18. The process of claim 1 wherein said boiling point of said compound is at least about 5°C lower than said oxygenate impurity.

19. The process of claim 18 wherein said converting step comprises contacting at least a portion of said hydrocarbonaceous stream with a catalyst comprising a member selected from the group consisting of metal and metal compound.

20. The process of claim 19 wherein said catalyst comprises at least one member selected from the group consisting of group 3 (IIIA) metal, group 3 (IIIA) metal compound, group 4 (IVA) metal, group 4 (IVA) metal compound, group 5 (VA) metal, group 5 (VA) metal compound, group 6 (VIA) metal, group 6 (VIA) metal compound, group 7 (VIIA) metal, group 7 (VIIA) metal compound, group 8 (VIIIA) metal, group 8 (VIIIA) metal compound, group 9 (VIIIA) metal, group 9 (VIIIA) metal compound, group 10 (VIIIA) metal, group 10 (VIIIA) metal compound, group 11 (IB) metal, group 11 (IB) metal compound, group 12 (IIB) metal, and group 12 (IIB) metal compound.

21. The process of claim 19 wherein said oxygenate impurity comprises dimethyl ether and said converting is carried out under conditions sufficient to convert said dimethyl ether to a mixture containing a member selected from the group consisting of methane, CO and CO₂.

22. The process of claim 19 wherein said catalyst comprises at least one member selected from the group consisting of group 11 (IB) metal and group 11 (IB) metal compound.

23. The process of claim 22 wherein said catalyst comprises Ag or a compound thereof.
24. The process of claim 19 wherein said catalyst comprises at least one of a group 11 (IB) metal or metal compound, and at least one inorganic oxide.
25. The process of claim 24 wherein said catalyst further comprises a group 12 (IIB) metal or metal compound.
26. The process of claim 25 wherein said catalyst further comprises a group 1 (IA) metal or metal compound.
27. The process of claim 26 wherein said group 11 (IB) metal or metal compound is selected from the group consisting of copper and copper compounds.
28. The process of claim 24 wherein said group 11 (IB) metal or metal compound is selected from the group consisting of silver and silver compounds.
29. The process of claim 24 wherein said inorganic oxide support comprises a member selected from the group consisting of silica, alumina, silica-alumina, zirconia, titania, aluminophosphate, and clay.
30. The process of claim 24 wherein said inorganic oxide comprises alumina.
31. The process of claim 24 wherein said catalyst comprises silver supported on alumina.
32. The process of claim 21 wherein said catalyst is a methanol synthesis catalyst.

33. The process of claim 32 wherein said methanol synthesis catalyst comprises copper, zinc oxide and alumina.
34. The process of claim 18 wherein no greater than about 1 wt% of said C_x olefin is converted by said converting step.
35. The process of claim 18 wherein no greater than about 0.1 wt% of said C_x olefin is converted by said converting step.
36. The process of claim 21 wherein said conditions sufficient to convert said dimethyl ether comprise temperatures ranging from about 300° to about 550°C, and pressures ranging from about 60 to about 3500 kPaa.
37. The process of claim 1 wherein said boiling point of said compound is at least about 10°C lower than said oxygenate impurity.
38. The process of claim 1 wherein said boiling point of said compound is at least about 50°C lower than said oxygenate impurity.
39. The process of claim 1 wherein said boiling point of said compound is at least about 5°C higher than said oxygenate impurity.
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40. The process of claim 39 wherein said converting is carried out in the absence of added hydrogen.
41. The process of claim 39 wherein said converting is carried out in the presence of added hydrogen.
42. The process of claim 39 wherein said converting comprises contacting at least a portion of said product stream with a supported metal catalyst comprising
i) at least one member selected from the group consisting of group 8 (VIII A)

metal, group 8 (VIII A) metal compound, group 9 (VIII A) metal, group 9 (VIII A) metal compound, group 10 (VIII A) metal, group 10 (VIII A) metal compound, group 11 (IB) metal, and group 11 (IB) metal compound, of the Periodic Table, and ii) at least one of a porous inorganic oxide and microporous crystalline molecular sieve, said converting taking place at conditions sufficient to convert said oxygenate impurity to at least one higher boiling compound.

43. The process of claim 42 wherein said contacting is carried out in the presence of hydrogen and said supported metal catalyst is a hydrogenation catalyst.

44. The process of claim 42 wherein said contacting is carried out in the absence of hydrogen.

45. The process of claim 42 said product stream comprises highly unsaturated C₂ to C₄ by-products comprising a member selected from the group consisting of an alkyne and an alkadiene

46. The process of claim 42 wherein additional amounts of a member selected from the group consisting of alkyne and alkadiene are added as necessary, to react during said converting with unreacted oxygenate.

47. The process of claim 42 wherein said alkyne comprises a member selected from the group consisting of acetylene, methyl acetylene, ethyl acetylene and dimethyl acetylene, and said alkadiene comprises a member selected from the group consisting of propadiene, 1,2-butadiene and 1,3-butadiene.

48. The process of claim 42 wherein the C₂ olefin fraction of said product stream or stream derived therefrom comprises at least 1 mppm of acetylene.

49. The process of claim 42 wherein the C₃ olefins fraction of said product stream or stream derived therefrom comprises at least 1 mppm of methyl acetylene and/or at least 1 mppm of propadiene.
50. The process of claim 42 wherein the C₄ olefins fraction of said product stream or stream derived therefrom comprises at least 1 mppm of a member selected from the group consisting of ethyl acetylene, dimethyl acetylene, 1,2-butadiene and 1,3-butadiene.
51. The process of claim 43 wherein said converting provides at least partial hydrogenation of said a member selected from the group consisting of alkyne and alkadiene by at least about 20%.
52. The process of claim 43 wherein said at least partial hydrogenation provides a member selected from the group consisting of ethylene, propylene and butene.
53. The process of claim 43 wherein said oxygenate impurity comprises dimethyl ether.
54. The process of claim 53 wherein wherein said product stream comprises C₃ to C₄ olefins and at least about 1 mppm oxygenate impurity.
55. The process of claim 54 wherein said catalyst comprises at least one member selected from the group consisting of group 10 (VIII) and group 11 (IB) metals.
56. The process of claim 42 wherein said catalyst comprises palladium.
57. The process of claim 42 wherein said catalyst comprises palladium and silver.

58. The process of claim 42 wherein said catalyst comprises at least one of i) at least one porous inorganic oxide selected from the group consisting of silica, alumina, silica-alumina, zirconia, titania, aluminophosphate and clay, and ii) at least one microporous crystalline molecular sieve selected from the group consisting of silicates, aluminosilicates, substituted aluminosilicates, aluminophosphates, and substituted aluminophosphates.
59. The process of claim 58 wherein said catalyst further comprises iii) at least one of a sulfur-containing moiety and oxygen-containing moiety.
60. The process of claim 42 wherein said converting is carried out in the liquid phase and comprises a temperature ranging from about 20°C to about 100°C, total pressures ranging from about 1140 kPaa to about 4240 kPaa (from about 150 psig to about 600 psig), LHSV ranging from about 0.1 to about 100, and a hydrogen/(alkyne+alkadiene) ratio ranging from about 0.1 to about 100 on a molar basis.
61. The process of claim 42 wherein said converting is carried out in the vapor phase and comprise a temperature ranging from about 20°C to about 600°C, total pressures ranging from about 102 kPaa to about 4240 kPaa (from about 0.1 psig to about 600 psig), GHSV ranging from about 100 to about 20,000, and hydrogen partial pressure ranging from about 0.001 psig to about 200 psig.
62. The process of claim 53 wherein said higher boiling compound is selected from the group consisting of acetone and methyl isopropyl ether.
63. The process of claim 53 wherein at least about 20% of said dimethyl ether in the product stream is converted during said converting step.

64. The process of claim 53 wherein at least about 50% of said dimethyl ether in the product stream is converted during said converting step.
65. The process of claim 53 wherein at least about 80% of said dimethyl ether in the product stream is converted during said converting step.
66. The process of claim 1 wherein said boiling point of said compound is at least about 10°C higher than said oxygenate impurity.
67. The process of claim 1 wherein said boiling point of said compound is at least about 50°C higher than said oxygenate impurity.
68. A process for at least partially removing dimethyl ether from a propylene-containing olefins stream which comprises converting at least a portion of said stream over a catalyst comprising metal and/or metal oxide, under conditions sufficient to selectively decompose said dimethyl ether to a mixture of methane, CO and CO₂, in the presence of said olefins without substantially converting said olefins.
69. The process of claim 68 wherein said catalyst comprises silver supported on alumina.
70. The process of claim 68 wherein said catalyst comprises copper, zinc oxide and alumina.
71. The process of claim 68 wherein said converting step is carried out in the absence of added hydrogen.
72. A process for at least partially removing oxygenate impurities from an olefin-containing stream produced by an oxygenate to olefin process which comprises:

contacting an oxygenate feedstream with an olefin generation catalyst under conditions sufficient to provide a first product stream which contains C₂ to C₄ olefins, C₂ to C₄ paraffins, hydrogen, methane, oxygenates comprising dimethyl ether, and highly unsaturated C₂ to C₄ by-products comprising a member selected from the group consisting of an alkyne and an alkadiene;

exposing at least a portion of said product stream or stream derived therefrom to a supported metal catalyst comprising i) at least one member selected from the group consisting of group 8 (VIII A) metal, group 8 (VIII A) metal compound, group 9 (VIII A) metal, group 9 (VIII A) metal compound, group 10 (VIII A) metal, group 10 (VIII A) metal compound, group 11 (IB) metal, and group 11 (IB) metal compound, of the Periodic Table, and ii) at least one of a porous inorganic oxide and microporous crystalline molecular sieve, said exposing taking place at conditions sufficient to convert said dimethyl ether to at least one higher boiling product; and

removing at least some of said higher boiling product.

73. The process of claim 72 wherein said exposing is carried out in the presence of hydrogen and said supported metal catalyst is a hydrogenation catalyst.

74. The process of claim 72 wherein said exposing is carried out in the absence of hydrogen.

75. The process of claim 72 wherein the C₃ to C₄ olefin fraction of said product stream or stream derived therefrom contains at least about 1 mppm oxygenates comprising dimethyl ether.

76. The process of claim 72 wherein said alkyne comprises a member selected from the group consisting of acetylene, methyl acetylene, ethyl acetylene and dimethyl acetylene, and said alkadiene comprises a member selected from the group consisting of propadiene, 1,2-butadiene and 1,3-butadiene.

77. The process of claim 76 wherein the C₂ olefin fraction of said product stream or stream derived therefrom comprises at least about 1 mppm of acetylene.

78. The process of claim 76 wherein the C₃ olefins fraction of said product stream or stream derived therefrom comprises at least about 1 mppm of methyl acetylene and/or at least 1 mppm of propadiene.

79. The process of claim 76 wherein the C₄ olefins fraction of said product stream or stream derived therefrom comprises at least about 1 mppm of a member selected from the group consisting of ethyl acetylene, dimethyl acetylene, 1,2-butadiene and 1,3-butadiene.

80. The process of claim 72 wherein said catalyst comprises at least one member selected from the group consisting of group 10 (VIII) and group 11 (1B) metals.

81. The process of claim 72 wherein said catalyst comprises palladium.

82. The process of claim 72 wherein said catalyst comprises at least one of i) at least one porous inorganic oxide selected from the group consisting of silica, alumina, silica-alumina, zirconia, titania, aluminophosphate and clay, and ii) at least one microporous crystalline molecular sieve selected from the group consisting of silicates, aluminosilicates, substituted aluminosilicates, aluminophosphates, and substituted aluminophosphates.

83. The process of claim 72 wherein said catalyst further comprises iii) a member selected from the group consisting of a sulfur-containing moiety and oxygen-containing moiety.

84. The process of claim 72 wherein said exposing conditions are carried out in the liquid phase and comprise a temperature ranging from about 20 °C to about 100 °C, total pressures ranging from about 150 psig to about 600 psig, LHSV ranging from about 0.1 to about 100, and a hydrogen/(alkyne +alkadiene) ratio ranging from about 0.1 to about 100 on a molar basis.

85. The process of claim 72 wherein said exposing conditions are carried out in the vapor phase and comprise a temperature ranging from about 20°C to about 600°C, total pressures ranging from about 0.1 psig to about 600 psig, GHSV ranging from about 100 to about 20,000, and hydrogen partial pressure ranging from about 0.001 psig to about 200 psig.

86. The process of claim 72 wherein said conversion of said dimethyl ether to at least one higher boiling product is at least about 20%.

87. The process of claim 72 wherein said conversion of said dimethyl ether to at least one higher boiling product is at least about 50%.

88. The process of claim 72 wherein said conversion of said dimethyl ether to at least one higher boiling product is at least about 80%.

89. The process of claim 72 wherein said at least one higher boiling product is formed from the reaction of dimethyl ether with a member selected from the group consisting of said alkyne, said alkadiene and said propylene.

90. The process of claim 89 wherein said alkyne comprises methyl acetylene, said alkadiene comprises propadiene, and said higher boiling product is selected from a member selected from the group consisting of acetone and methylisopropyl ether.

91. The process of claim 72 wherein additional amounts of a member selected from the group consisting of alkyne and alkadiene are added as necessary, to react during said exposing with unreacted oxygenate.

92. The process of claim 73 wherein said exposing is carried out under conditions sufficient to effect at least partial hydrogenation of said a member selected from the group consisting of alkyne and alkadiene at a conversion of at least about 20%.

93. The process of claim 73 wherein said exposing is carried out under conditions sufficient to effect at least partial hydrogenation of said member selected from the group consisting of alkyne and alkadiene at a conversion of at least about 50%.

94. The process of claim 73 wherein said exposing is carried out under conditions sufficient to effect at least partial hydrogenation of said a member selected from the group consisting of alkyne and alkadiene at a conversion of at least about 80%.

95. The process of claim 73 wherein said exposing is carried out under conditions sufficient to effect at least partial hydrogenation of said member selected from the group consisting of alkyne and alkadiene so as to provide a member selected from the group consisting of ethylene, propylene and butene.

96. The process of claim 72 wherein said removing of said higher boiling product is carried out by fractionating in a distillation column.

97. A process for at least partially removing oxygenate impurities from an olefin-containing stream produced by an oxygenate to olefin process which comprises:

contacting an oxygenate feedstream with an olefin conversion catalyst under conditions sufficient to provide a first product stream which contains water, C₅+ organic compounds, ethylene, propylene, butylenes, oxygenates comprising dimethyl ether, and unsaturated C₂ to C₄ by-products comprising a member selected from the group consisting of an alkyne and an alkadiene;

at least partially removing said water, ethylene, butylenes and C₅+ organic compounds from said first product stream to provide a second product stream enriched in propylene relative to said first product stream, and comprising a member selected from the group consisting of an alkyne and an alkadiene, and containing dimethyl ether;

exposing at least a portion of said second product stream in the presence of hydrogen to a hydrogenation catalyst comprising i) at least one member selected from the group consisting of group 8 (VIII A) metal, group 8 (VIII A) metal compound, group 9 (VIII A) metal, group 9 (VIII A) metal compound, group 10 (VIII A) metal, group 10 (VIII A) metal compound, group 11 (IB) metal, and group 11 (IB) metal compound, of the Periodic Table, and ii) a member selected from the group consisting of a porous inorganic oxide and microporous crystalline molecular sieve, said exposing taking place at conditions sufficient to simultaneously effect 1) conversion of said dimethyl ether to at least one higher boiling product, and 2) at least partial hydrogenation of said member selected from the group consisting of alkyne and alkadiene; thereby providing a third product stream; and

removing said higher boiling product from said third product stream.

98. The process of claim 1 wherein said converting step is carried out in the presence of H₂O with an acid catalyst under conditions sufficient to at least partially convert said oxygenate impurity to its corresponding alcohol(s).

99. The process of claim 98 wherein said oxygenate impurity is dimethyl ether and said corresponding alcohol is methanol.

100. The process of claim 99 wherein said product stream comprises propane.
101. The process of claim 99 wherein said catalyst is a non-shape selective acid catalyst.
102. The process of claim 101 wherein said acidic catalyst comprises gamma-alumina.
103. The process of claim 99 wherein said conditions comprise a temperature ranging from about 300°C to about 800°C and a weight ratio of said dimethyl ether to said H₂O of no greater than about 2.5.
104. The process of claim 99 wherein said conditions comprise a temperature of at least about 500° C and a weight ratio of said dimethyl ether to said H₂O ranging from about 1.2 to about 2.5.
105. The process of claim 99 wherein said conditions comprise a temperature ranging from about 600°C to about 800° C and a weight ratio of said dimethyl ether to said H₂O ranging from about 0.5 to about 2.5.
106. The process of claim 99 wherein said conditions provide at least about 25% to about 95% conversion of said dimethyl ether to methanol.
107. The process of claim 106 wherein said conditions provide at least about 90% conversion of said dimethyl ether to methanol.
108. The process of claim 107 wherein said conditions provide at least about 92% conversion of said dimethyl ether to methanol.
109. The process of claim 100 wherein said propane-containing stream is derived from an oxygenate to olefins conversion process effluent.

110. The process of claim 99 wherein at least some of said H₂O is steam.

111. The process of claim 99 wherein at least some of said H₂O is separated along with said methanol in said separation step.